XXVI. *On the Law of Expansion of Superheated Steam.*

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THE following experiments have been undertaken to verify the law of expansion for superheated steam indicated in a previous paper*.

The earliest experiments on the subject were made by Mr. FROST in America, but without sufficient accuracy to be of scientific value. Mr. SIEMENS has also experimented on the expansion of steam isolated from water; his results give a much higher rate of expansion for steam than for ordinary gases; but, owing to the obvious defects of Mr. SIEMENS's method of conducting the experiments, we consider that his results are not reliable.

For gases, the rate of expansion is expressed by the formula, for constant volume,

$$\frac{P}{P_1}=\frac{E+t}{E+t_1}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1.)$$

where E is a constant derived from experiment and determined by REGNAULT to be 459 in the case of air In the paper alluded to, it was shown that, with a certain proviso, the rate of expansion of superheated steam nearly coincided with that of air. Within a short distance of the maximum temperature of saturation, the rate of expansion of steam was found to be exceedingly variable; near the saturation-point it is higher than that of air, and it decreases as the temperature is increased until it becomes sensibly identical with that of air. The results on which this law was based were too limited in their range for much numerical accuracy in the constants deduced.

Hence it has been our object in the present paper to supply the deficiency in the previous one, by affording experimental data of the expansion of steam at higher temperatures and with a greater range of superheating than was possible with the apparatus employed in ascertaining the density of steam. The results obtained in these later researches, however, confirm the general law deduced from the previous ones.

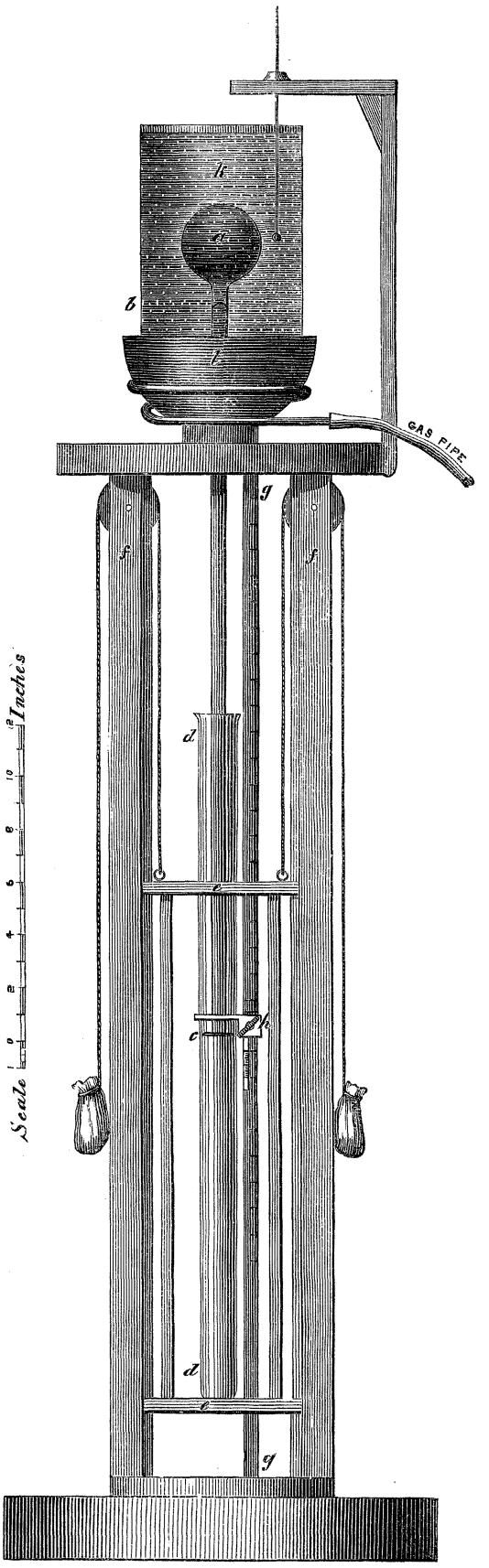
The annexed diagram represents the experimental apparatus employed where the pressures did not exceed that of the atmosphere. It consists of a glass globe a, about three inches in diameter, and with a stem about thirty-five inches long. The capacity of this globe was known to a point b on the stem, where a piece of fine platinum wire was twisted round it to mark accurately the level to which the mercury column in the stem was to be brought to maintain a constant volume in the globe. The stem dipped below into the

* "Experimental Researches on the Density of Steam at different Temperatures, and to determine the Law of Expansion of Superheated Steam," Phil. Trans. 1860, p. 185.

$1\frac{1}{4}$-inch tube *d*, which was supported on a frame of wood *e e*, sliding up and down vertically on the larger frame *f f*, on which the apparatus was supported. The frame *e e*, and the tube *d*, were balanced by cords passing over pulleys in the top of the frame, and weighted by bags filled with small pieces of iron. In this way the tube *d* could be adjusted with the greatest facility, so as to maintain the upper level of the mercury column at a constant position. To read the lower and variable level of the column, a rod *g g*, graduated into tenths of an inch, was fixed vertically, carrying a finger and vernier, *h*, which could be made to coincide accurately with the top of the meniscus of mercury, *c*.

For heating the globe, a glass bath, *k*, containing oil, was provided, fixed in an outer iron mercury bath, *l*. This was heated by a coil of gas-jets, and the oil was stirred continually, excepting at the instant of adjusting the upper level of the column to the level of the platinum wire. The globe was fixed in the oil-bath by a stuffing-box.

The method of conducting the experiments was as follows. The globe *a* was filled with dry and warm mercury, the air-bubbles being extracted from time to time by an air-pump. It was then inverted to form a Torricellian vacuum. A small glass globule of water was then inserted, the platinum wire fixed in its place, and an india-rubber cap fitted over the extremity of the stem. It was then transferred to its place in the oil-bath, and fixed there. The india-rubber cap was replaced by an open glass cistern, so that the glass tube *d* could be elevated to its position. The gas-jets were lighted, and the temperature raised to 300°. From this point the levels of the column were read off at intervals of 50° until the temperature of saturation was reached. The levels were



taken in a series of descending temperatures, to avoid the influence of steam boiling out of the mercury as the temperature rose, and to eliminate the effect of the cohesion of the glass on the water, as explained in our previous paper on the Density of Steam.

Capacity of the Globe.

Twelve cubic inches of mercury were measured into the globe, and a file-mark made on the stem.

Below the first file-mark, at a distance of 14·45 inches, another file-mark was made to afford a fixed point for ascertaining the correspondence of the upper file-mark with the readings on the fixed graduated rod or cathetometer.

Correction of Readings.

Let a be the reading on the fixed rod of the level of the column; b be the reading of the lower file-mark on the globe-stem. Then

$+b-a$=the height of the column of mercury in the globe-stem.

To correct this for temperature, $7\frac{1}{2}$ inches of mercury, included in the oil-bath and its stuffing-box, were corrected for the temperature of the oil, and the remainder for the temperature of the atmosphere at the time.

By deducting the column so corrected from the reading of the barometer at the time, the total pressure in the globe is obtained.

The readings of the thermometer are corrected for the portion out of the oil-bath.

The pressure of the vapour of mercury is calculated from data supplied with great courtesy by M. REGNAULT, and embodying the results of unpublished experiments. The pressure of this vapour is assumed to be the same as that in a vacuum, as the vapour in the globe remains still for a sufficient time (it is believed) for saturation to take place. In this view we have been strengthened by M. REGNAULT'S opinion.

By deducting the pressure of mercury vapour from the total pressure in the globe, the pressure of the steam is obtained.

Experiment I.

0·285 grain of water introduced into globe.

Time.	Temperature in oil-bath, Fahr.	Cathetometer, in inches.	Column of mercury, in inches.	Temperature of air, Fahr.	Remarks.
h m					
4 46	250°	10·96	25·57	58°	Barometer read 30·33 inches, or, corrected to 32° F., 30·27 in.
4 55	250	10·96	25·57		
5 8	300	11·40	25·13		The lower file-mark read 22·08 inches on the cathetometer.
5 14	300	11·38	25·15		
5 17	300	11·40	25·13		
5 20	300	11·40	25·13		
5 37	250	10·97	25·56		
5 40	250	10·96	25·57		
6 0	200	10·63	25·90		
6 8	200	10·60	25·93		
6 13	200	10·60	25·93		
6 45	150	10·28	26·25		
6 50	150	10·25	26·28		
7 25	100	7·90	28·63		
7 30	100	7·87	28·66	57	Barometer read 30·36 inches, or, corrected to 32° F., 30·30 inches.

Summary of Results.

Temperature, Fahr.	Mean column of mercury, in inches.	Mean column corrected to 32°.	Total pressure in globe, in inches.	Volume of globe corrected for expansion of glass, in grs. of water.	Pressure of vapour of mercury, in inches.	Pressure of steam, in inches.	Value of E.
302°·88	25·13	24·89	5·38	3045·5	0·1736	5·21	474·48
251·64	25·55	25·34	4·94	3043·4	0·066	4·87	450·11
200·74	25·92	25·75	4·54	3041·2	0·024	4·52	428·88
150·18	26·26	26·13	4·17	3039·1	0·008	4·16	
100·00	28·64	28·54	1·76	3037·0	0·003	1·76	

Experiment II.

0·405 grain of water introduced into globe.

Time.	Temperature in oil-bath, Fahr.	Cathetometer, in inches.	Column of mercury, in inches.	Temperature of air, Fahr.	Remarks.
h m					
4 30	300°	13·43	23·16	59°	Barometer read 30·38 inches throughout the experiment, or, corrected to 32° F., 30·31 inches. Lower file-mark read 22·14 inches on the cathetometer.
4 40	300	13·45	23·14		
4 45	302	13·50	23·09		
4 50	300	13·49	23·10		
5 10	250	12·90	23·69		
5 16	250	12·90	23·69		
5 20	250	12·90	23·69		
5 40	200	12·43	24·16	60	
5 45	200	12·43	24·16		
5 50	200	12·43	24·16		
6 10	150	11·94	24·65		
6 15	150	11·98	24·61		
6 20	150	11·97	24·62		
6 25	150	11·97	24·62		

Summary of Results.

Temperature, Fahr., corrected.	Mean column of mercury, in inches.	Mean column corrected to 32°.	Total pressure in globe, in inches.	Volume of globe corrected for expansion of glass, in grs. of water.	Pressure of vapour of mercury, in inches.	Pressure of steam, in inches.	Value of E.
302°·88	23·11	22·87	7·44	3045·5	0·174	7·27	455·57
251·64	23·69	23·49	6·82	3043·4	0·066	6·75	
200·74	24·16	23·99	6·32	3041·2	0·024	6·30	
150·18	24·62	24·49	5·82	3039·1	0·008	5·81	443·86

In the readings at 251·64 some error seems to have crept in. In deducing E, the readings at 302·88 and 200·74 are therefore taken.

Experiment III.

0·545 grain of water introduced into globe.

Time.	Temperature of oil-bath, Fahr.	Cathetometer, in inches.	Column of mercury, in inches.	Temperature of air, Fahr.	Remarks.
h m					
3 55	299°	16·05	20·26	59°	Barometer read 30·13 inches, or, corrected to 32° F., 30·06 inches throughout the experiment.
4 0	300	16·05	20·26		
4 5	300	16·05	20·26		Lower file-mark read 21·86 inches on the cathetometer.
4 33	250	15·33	20·98		
4 40	250	15·32	20·99	60	
4 45	250	15·34	20·97		
5 3	200	14·66	21·65		
5 10	200	14·66	21·65		
5 14	200	14·65	21·66	61	
5 32	150	13·05	23·26	.....	Condensation in globe.
5 37	150	13·10	23·21		
5 43	150	13·05	23·26		

Summary of Results.

Temperature, Fahr., corrected.	Mean column of mercury, in inches.	Mean column, corrected to 32°.	Total pressure in globe, in inches.	Volume of globe corrected for expansion of glass, in grs. of water.	Pressure of vapour of mercury, in inches.	Pressure of steam, in inches.	Value of E.
302°·88	20·26	20·03	10·03	3045·5	0·174	9·86	466·85
251·64	20·98	20·78	9·28	3043·4	0·066	9·21	451·94
200·74	21·65	21·49	8·57	3041·2	0·024	8·55	109·74
150·18	23·25	23·12	6·94	3039·1	0·008	6·93	

Experiment IV.

0·53 grain of water introduced into globe.

Time.	Temperature in oil-bath, Fahr.	Cathetometer, in inches.	Column of mercury, in inches.	Temperature of air, Fahr.	Remarks.
h m					
12 0	300°	16·62	20·63	65°	Barometer read 30·17 to 30·18 inches during experiment, the corrected reading being 30·09 inches.
12 5	300	16·62	20·63		
12 15	300	16·61	20·64		Lower file-mark read 22·80 inches on the cathetometer.
12 44	250	15·93	21·32	65	
12 51	250	15·92	21·33		
1 5	250	15·92	21·33		
1 38	200	15·27	21·98		
1 45	200	15·28	21·97		
1 52	200	15·28	21·97	66	
2 35	150	13·95	23·30		
2 47	150	14·00	23·25		
3 0	150	14·01	23·24		
3 5	150	14·00	23·25		
3 20	165	14·80	22·45		
3 23	165	14·79	22·46	67	

Summary of Results.

Temperature, Fahr., corrected.	Mean column of mercury, in inches.	Mean column, corrected to 32°.	Total pressure in globe, in inches.	Volume of globe corrected for expansion of glass, in grs. of water.	Pressure of vapour of mercury, in inches.	Pressure of steam, in inches.	Value of E.
302°·88	20·63	20·39	9·70	3045·5	0·174	9·53	464·83
251·64	21·33	21·12	8·97	3043·4	0·066	8·90	460·79
200·74	21·97	21·80	8·29	3041·2	0·024	8·27	378·33
165·45	22·46	22·31	7·78	3039·7	0·011	7·77	
150·18	23·25	23·11	6·98	3039·1	0·008	6·97	

Experiment V.

0·875 grain of water introduced into globe.

Time.	Temperature in oil-bath, Fahr.	Cathetometer, in inches.	Column of mercury, in inches.	Temperature of air, Fahr.	Remarks.
h m					
1 10	300°	23·25	14·03	63°·5	Barometer read 30·13 inches, or, corrected to 32° F., 30·06 inches.
1 15	301	23·27	14·01		Lower file-mark read 22·83 inches on the cathetometer.
1 20	300	23·26	14·02		
1 25	300	23·25	14·03		
1 45	250	22·14	15·14		
1 50	250	22·11	15·17		
2 0	250	22·14	15·14		
2 5	250	22·13	15·15		
2 35	200	21·00	16·28		
2 41	200	21·00	16·28		
2 45	200	21·01	16·27	63·5	
2 50	200	21·00	16·28		
3 5	180	20·50	16·78		
3 15	180	20·49	16·79		
3 20	180	20·49	16·79	64·0	
3 35	165	17·27	20·01		
3 45	167	17·85			
3 50	165	17·32	19·96		
4 0	165	17·30	19·98		

Summary of Results.

Temperature, Fahr., corrected.	Mean column of mercury, in inches.	Mean column, corrected to 32°.	Total pressure in globe, in inches.	Volume of globe corrected for expansion of glass, in grs. of water.	Pressure of vapour of mercury, in inches.	Pressure of steam, in inches.	Value of E.
165°·45	19·98	19·84	10·22	3039·7	0·011	10·21	
180·72	16·79	16·65	13·41	3040·6	0·016	13·39	
200·74	16·28	16·13	13·93	3041·2	0·024	13·91	430·90
251·64	15·15	14·97	15·09	3043·4	0·066	15·02	460·28
302·88	14·02	13·80	16·26	3045·5	0·174	16·09	

Summary of Results.

The law of expansion of gaseous bodies is expressed by the formula

$$\frac{E+t}{E+t_1}=\frac{PV}{P_1V_1},$$

$$\therefore E=\frac{PVt_1-P_1V_1t}{P_1V_1-PV},$$

where E is a constant. The values of E thus deduced have been placed in the last column of the foregoing Tables. They show a decreasing rate of expansion from the saturation-point upwards until (at a certain increase of temperature) the rate of expansion coincides with that of a perfect gas.

Taking from the preceding Tables the two results, which in each case represent the rate of expansion at the greatest distance from the saturation-point, we have the following values of E:—

(1)	474·48
	450·11
(2)	455·57
	443·86
(3)	466·85
	451·94
(4)	464·83
	460·79
(5)	460·28
	9)4128·71
Mean value of E=	458·74

The value of E for air, as ascertained by REGNAULT, is 459. That assumed for a perfect gas by RANKINE is 461·2.

Hence the conclusion which we suggested in our previous paper has been satisfactorily demonstrated in more carefully conducted experiments, and the rate of expansion of superheated steam is shown to be almost identical with that of air and other permanent gases, if calculated at temperatures not too close to the maximum temperature of saturation.